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MALARIAL PIGMENT (HEMATIN) AS A FACTOR IN THE PRODUCTION OF THE MALARIAL PAROXYSM.*

By Wade H. Brown, M. D.

It is remarkable that, from the enormous amount of investigation that has centered about the malarial parasite and its relation to malarial fevers, there has come no clear exposition of the mode of production of the various phenomena of the malarial paroxysm. It is true that these phenomena have been ascribed to the presence in the circulation of some toxic substance, or substances, elaborated by the malarial parasite, and that the blood at the time of the segmentation of the parasite has been shown to possess toxic properties. Still, as far as I know, the nature of these toxic agents remains unknown, as no one has clearly demonstrated the presence of any definite substance, which, when introduced into the circulation, could reproduce the symptom complex of the malarial paroxysm. The observations embodied in this report are offered, therefore, with the hope of shedding some light upon the question.

In the course of some work on hematin metabolism, it was noted that a rabbit that had received an intravenous injection of alkaline hematin developed a very pronounced shaking chill, strikingly like that of malaria. As the author has attempted to show in a previous paper,[1] the pigment elaborated from the hemoglobin of the red blood corpuscle by the malarial parasite

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The first seven experiments of this investigation were done in the Pathological Laboratory of the University of Wisconsin, Madison, Wis.

[1] W. H. Brown, *Jour. Exper. Med.*, 1911, xiii, 290.

and liberated into the circulation of the host at the time of segmentation of the parasite is undoubtedly hematin. It at once appeared possible, therefore, that we might find in this substance one of the hypothetical toxins operative in malaria. The investigation of this question now embraces a series of ninety observations upon the effect of the intravenous injection of alkaline hematin, eighteen rabbits having been used for test purposes.

TECHNIQUE.

Materials Used and Their Preparation.—The hematin used was derived from three sources, rabbit blood, dog blood, and ox blood, but in all cases it was prepared by the Schalfijew process. The solutions for injection were made in 0.85 per cent. salt solution containing 1.5 or 2 per cent. bicarbonate of sodium. The strength of the hematin employed has varied from 1.5 to 5 milligrams per cubic centimeter. The hematin was added to the sterile solvent and heated to 100° C. for five to ten minutes, and was then allowed to stand for twelve to twenty-four hours, when it was again heated and, while still hot, filtered into sterile flasks. The subsequent treatment of these solutions has varied somewhat. Solutions prepared thus, and again heated to 100° C. for five to ten minutes have apparently remained sterile. In a few instances, however, the filtered solution has been autoclaved to insure sterility.

It has been found extremely difficult to prepare hematin solutions of absolutely uniform character. With a given preparation of hematin and with the same technique in the preparation of the solutions, two distinct types of solution may be obtained: one, a perfectly clear, deeply colored solution that even under the microscope shows very few particles of pigment suspension, and on standing shows no precipitation in the flask; the other, a turbid solution that appears chocolate brown in thin layers and under the microscope shows myriads of pigmented particles and droplets floating in an only faintly colored fluid. Much of this pigment is precipitated on allowing the solution to stand. This latter "colloidal" type of solution or suspension, manifests all the optical properties of

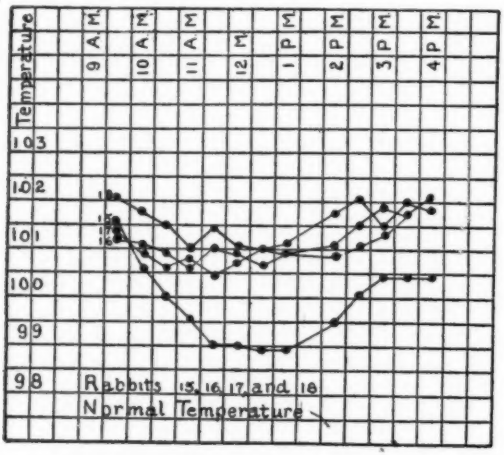
an alkaline hematin solution and the suspended pigment readily passes through Schleicher and Schüll filter paper No. 597 which has been used as the routine filter. With different preparations of hematin these variations in solubility are continually appearing. Reference is made to this feature of the hematin solution to indicate the difficulty in maintaining absolutely uniform experimental conditions and accurate dosage.

Experimental Procedure.— Briefly, the experiments have been conducted according to the following plan: The animals were accustomed to laboratory surroundings by being kept in cages from one to two days before any observations were made. The normal temperature curve of each animal was then established by rectal temperature, taken every half hour from 8 or 9 A. M. until 3 or 4 P. M., the time to be covered by subsequent experiments. As it seemed probable that the sodium bicarbonate salt solution used as the solvent for hematin might produce some toxic manifestations when injected intravenously, the action of this solution was determined in a number of instances, usually in such doses as were subsequently to be administered with the hematin. While these control tests were usually made prior to the injection of hematin, some such tests followed the administration of hematin. The animals were next given intravenous injections of alkaline hematin at 8 or 9 A. M., and the resulting phenomena were noted, the temperature being taken as previously, although fifteen-minute observations were frequently made.

Dose of Hematin.—It is evident that the question of dosage in such a series of experiments is one of prime importance. To carry out the object of these experiments it is quite essential that the dose of hematin employed be somewhat comparable to that liberated into the human circulation at the time of segmentation of a generation of parasites. While there is no evidence to show that all the hemoglobin of the infected red corpuscles is decomposed to form hematin, if we may assume that such is the case, and, further, that a 1 to 5 per cent. infection of red blood corpuscles is not uncommon, we have sufficient data upon which to base a calculation of the approx-

imate amount of hematin liberated into the human host with the segmentation of a given generation of parasites. Basing our calculations on the presence of 8.5 grams of hemoglobin per kilo of body weight, and 4.47 per cent. of hematin in hemoglobin,[2] we find that in a 1 per cent. infection of the red blood corpuscles approximately 3.7 milligrams of hematin per kilo of body weight would be liberated. In my experiments the dosage has varied from 1.3 milligrams to 28 milligrams per kilo of body weight, given in single or in divided doses, corresponding roughly to an infection of 0.3 to 7.5 per cent. of the red blood corpuscles.

Normal Temperature of the Rabbit.—In undertaking an investigation which must necessarily deal so largely with variations in the temperature of the experimental animal, it is im-



TEXT-FIG. 1. Normal temperature of four rabbits during the period of the experiments.

perative that the basis of comparison between normal and abnormal fluctuations of temperature be as free from objection as possible. Unfortunately, the temperature of different rabbits

[2] Olof Hammarsten, A Text Book of Physiological Chemistry, translated by Mandel, New York, 1901, p. 139. These figures are probably high.

varies widely, even when kept under exactly the same conditions. In apparently normal animals I have found the individual extremes between 98° and 103° F. Likewise, the fluctuations of temperature in a given animal may be quite considerable, but usually follow a fairly definite course.

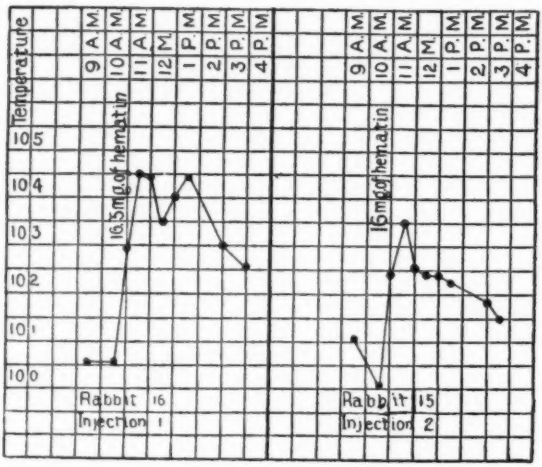
The course and fluctuations of temperature of the normal rabbit under experimental conditions, as well as the individual difference in temperatures, are shown in text-figure 1. This chart shows the normal temperatures recorded for rabbits 15, 16, 17, and 18. The first three animals were from the same litter, about three-quarters grown, and weighed 1,600 to 1,700 grams. Number 18 was full grown and weighed 1,840 grams. All the records were taken at the same time and all conditions were as nearly alike as possible. While three of these curves coincide closely, the fourth shows an extremely low and irregular curve of temperature. It should be noted that the temperature in all instances has a downward trend during the morning hours, and does not show an upward tendency until about noon, when there is a gradual rise, which ultimately reaches as high as the temperature at the first observation or even higher. This temperature curve has been fairly constant in my entire series of experiments.

Effect of Hematin upon Temperature.—If, for purposes of comparison, we adopt the classical division of the malarial paroxysm into a cold stage, a hot stage, and a stage of sweating, with the concomitant symptoms belonging to each, certain of these manifestations are capable of accurate measurements in an experimental animal, while others may be determined with a fair degree of accuracy by close observations, and still others are wholly indeterminable. Of prime importance among these phenomena of the malarial paroxysm is the question of fever.

In estimating the temperature effects, in all instances at least three facts are to be taken into consideration: the nature of the effect, the degree of the effect, and the duration of the effect. While it has been possible to assemble much of the data concerning the effects of hematin upon the temperature in an appended table which shows the abbreviated protocols of the

entire series of experiments, it must be fully appreciated that such tabulations of statistics are wholly inadequate to present many features of the experiments that are equally as important as those thus presented, and attention will be especially directed to such features. Further, as can be seen from these tables, it has been the object of the author to study effects in individual animals with a variety of doses, as occasion suggested, rather than to mould all the experiments to a single type or plan, for it became evident early in this investigation that individual peculiarities of the animals played a prominent rôle in the results obtained.

Without exception, every dose of hematin administered has elicited a definite temperature response. With but three exceptions, this response has been characterized by a sharp rise in temperature, reaching the fastigium in about an hour and a

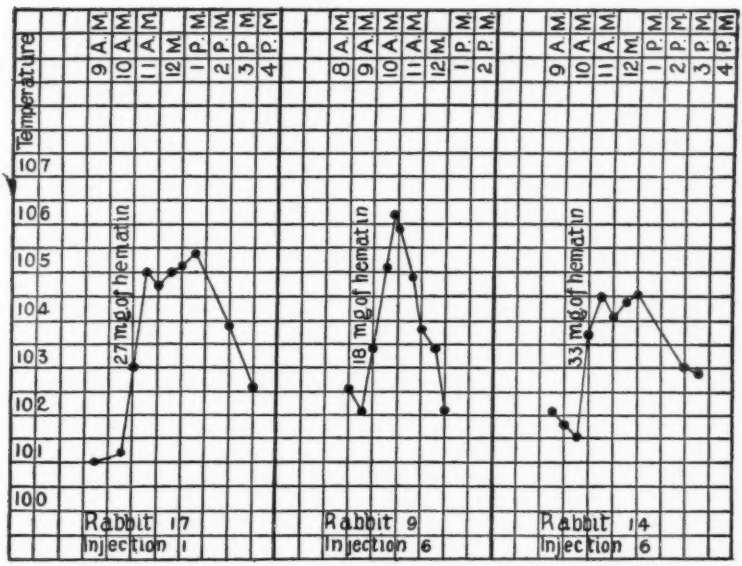


TEXT-FIG. 2. The usual types of temperature curve following injections of hematin.

quarter. The further course was somewhat variable, although in most cases with a dose of 15 milligrams, or less, per kilo, there was a rather sharp fall of temperature for thirty minutes

to one hour, followed by a secondary rise of variable extent and duration or a very gradual decline requiring several hours to reach normal again. Two such temperature curves are shown in text-figure 2.

These curves are subject to innumerable variations depending upon the dose, the stage of the experiment, and upon the individual peculiarities of animals. Some of the more important variations are an accentuation and prolongation of the secondary rise, usually shown with initial and large doses, or a defervesence that is almost as sharp as the rise in temperature. A third variation, which includes the three exceptions previously noted, is met with in instances of marked intoxication and is characterized by an initial drop in temperature with a subsequent rise. All three of these modifications are illustrated in text-figure 3.



TEXT-FIG. 3. Variations in the temperature curve following large doses of hematin or repeated injections of hematin.

The extent of the temperature elevation is, within certain limits, proportional to the amount of hematin injected. The temperature effect, being very slight with small doses, increases with the dose, until we begin to obtain signs of an over-intoxication when the elevation may be much less than with smaller doses, the optimum dose usually being between 10 and 15 milligrams per kilo of body weight. The elevation of temperature obtained with such optimum doses is from 3° to 3.5° F., and it is exceptional that a greater rise is reached. Occasionally, however, the temperature may rise 4° F. or even higher in highly susceptible animals. The greatest elevation recorded in my series of experiments was 4.9° F. in animal No. 9, with a dose of 18 milligrams of hematin per kilo.

In well-marked reactions, the temperature usually returns to within the normal range in the course of three to five hours. With large or initial injections of hematin, the period of elevated temperature is more prolonged than under other circumstances and seldom reaches normal in less than four hours, occasionally requiring as much as six hours. Exceptionally, the return to normal may be rapid (text-figure 3).

The method of administration also plays an important part in the results. A given dose of hematin injected in two or three fractional doses at intervals of fifteen to thirty minutes produces a much more marked elevation of temperature than when given at a single injection, an effect that is well shown in rabbit 13. This is particularly true of the smaller, or optimum doses, while with larger doses the increased potency may be manifested by a slowing of the rise of temperature, a cessation of the rise, or even a fall upon the injection of the second fraction, as illustrated in rabbit 12.

Neither the source of the hematin nor the type of solution seems to play an important part in the results that I have obtained. That is, there has been but slight difference between the action of rabbit, dog, or ox hematin, or between the action of the perfectly clear hematin solution and that containing much finely divided hematin in suspension.

However, a few tests seem to indicate that solutions of hem-

atin gradually lose their pyrogenic properties with age or when subjected to high and prolonged temperature. This apparent decrease may be seen by comparing the results obtained in rabbit 7, injection 3, and rabbits 8, 10, and 11. Further, it can readily be imagined that all animals will not be found equally susceptible to the toxic action of hematin. A few will exhibit a marked sensitiveness and a few will be found extremely resistant, the optimum dose in the one producing but slight effect in the other. This variation in susceptibility was strikingly illustrated by animals 13 and 14 which were under observation at the same time. Rabbit 13 was a typically resistant animal, and rabbit 14 was highly sensitive.

Effect of Sodium Bicarbonate Salt Solution upon the Temperature.—Animals injected with the bicarbonate salt solution alone, for purposes of control, almost invariably showed an elevation of temperature in proportion to the size of the dose, and about one-third to one-half the elevation produced with an equal amount of hematin solution, depending somewhat upon the concentration of the hematin in the solution. With small doses of the control medium, the fluctuations of temperature were usually within what might be termed the normal range and were such that it is difficult to say whether they are more than incidental to the process of injection. Large doses may produce a rise in temperature corresponding approximately to the over-intoxicating effect of large doses of hematin. In such instances, however, other features of the clinical picture will distinguish sharply between the two cases. In all instances, therefore, there were distinct differences between the action of the sodium bicarbonate salt solution and the action of the hematin solution, such that there can be no question as to the part played by the hematin in these experiments.

Other Phenomena of the Hematin Paroxysm.—Apart from the elevation of temperature in the experimental animal, the paroxysm of hematin intoxication presents other features which are of equal importance and show a strong resemblance to corresponding phenomena of the malarial paroxysm. For the first fifteen to twenty minutes following the injection of

hematin, the rabbit usually manifests a slight degree of restlessness, then crouches in a corner of the cage. In the second stage of the paroxysm the vessels of the ears contract giving to the shaved ears a pale and cyanotic hue, while at the same time the ears become decidedly cold. In pronounced cases the surface temperature (temperature of the ears) may be more than 30° F. below the rectal temperature. The lowest temperature recorded in this series of experiments was 63.5° F. with a room temperature of 62.5° F., and a rectal temperature of 105° F. During this stage the animal's ears usually lie on its back, and the hair tends to become erect, presenting the picture of an animal that is cold. Meanwhile, the rabbit shows convulsive tremors or shivering, but rarely any continued or pronounced shaking. This stage of chill lasts from forty-five minutes to one hour, and is terminated rather abruptly by a dilation of the superficial vessels, the ears rapidly becoming flushed and hot. The animal now moves about the cage or stretches out and remains quiet. Further than this, the third or hot stage of the paroxysm possesses no especial symptoms and its limit can be fixed only by the course of the temperature, which may remain well above normal for several hours, or sink to normal within an hour. During the third stage and the latter part of the second stage of the paroxysm the animal shows a pronounced thirst which is undoubtedly referable to the febrile condition.

The most striking and at the same time the most constant of all these symptoms are the contraction and dilatation of the superficial vessels associated with the corresponding lowering and elevation of the surface temperature.

The contrast between the symptoms of the animal injected with hematin and those of control animals is quite as sharp as in the instance of the temperatures. With doses of hematin sufficiently large to produce pronounced symptoms of the type described, corresponding doses of sodium bicarbonate salt solution produce practically no recognizable effect. There may be a suggestive or very transient change in the surface vessels and the temperature, but nothing that is definite or constant. When,

however, larger doses, *e. g.,* ten cubic centimeters per kilo, are given, phenomena simulating the picture of hematin intoxication may be elicited, but the changes are not so definite or constant.

If now we correlate these symptoms with the temperature curve, we find that the elevation of temperature during the first stage is slight, and that the second stage of the paroxysm corresponds closely with the period of rising temperature, the initial drop coinciding sharply with the vascular dilatation and flushing of the ears and the elevation of the surface temperature. The third or hot stage, as previously noted, corresponds to the duration of the temperature above normal.

As in the case of the temperature, all other phenomena of hematin intoxication seem to be exaggerated when a given dose of hematin is divided into several fractional doses, the cycle of phenomena following closely consequent changes in the temperature curve.

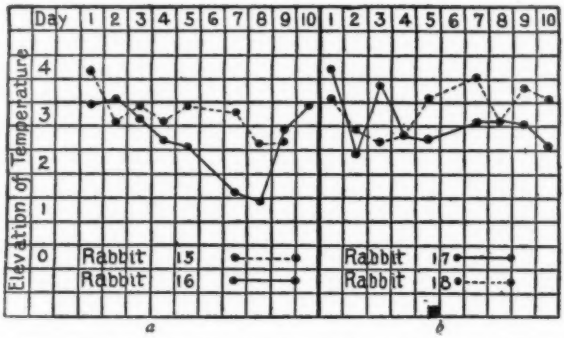
It must be pointed out, however, that the prominence of these paroxysmal phenomena and the degree of elevation of the temperature are by no means always parallel. The toxic paroxysmal phenomena may be present to a high degree in an animal that shows only a slight elevation of temperature, and in most instances such a condition is to be regarded as evidence of over-intoxication.

Acquired Resistance.—Early in the course of these experiments it became evident that repeated injections of a given dose of hematin in the same animal did not give uniform results. The results, however, were of such a nature as to suggest that the animal acquired a certain degree of tolerance which, in turn, might be broken when the intoxication was pushed sufficiently. To determine this point the following experiment was carried out.

Experiment.—Four rabbits, weighing respectively 1,600, 1,650, 1,790, and 1,840 grams, were injected on ten successive days with a solution of ox hematin containing 5 mg. of hematin to 1 c.c. The first two animals received 10 mg. of hematin per kilo of body weight, and the other two received 15 mg. per kilo. Rectal temperatures were recorded every half hour.

The results are shown in text-figure 4. In *a* is shown the

differences of elevation of temperature on successive days of the two animals receiving ten milligrams per kilo, and in *b* those receiving fifteen milligrams per kilo.



TEXT-FIG. 4. Variations in the elevation of the temperature with repeated injections of a given does of hematin.

While the curve of temperature reaction in each case is extremely irregular, it is in general characterized by a tendency towards a decrease, which in the instance of animals 16 and 17 persists throughout the experiment. With animals 15 and 18, however, a second phase of increased reaction is developed. These animals also exhibited the most marked symptomatic effects throughout the experiment. If the temperature curve alone be considered, it is certain that the tendency is toward a decreasing response to successive injections of hematin, and this I have found to be true in other experiments. If we take into consideration other evidence of intoxication, however, as in animals 15 and 18, this decrease seems referable not so much to a tolerance as to over-intoxication. Again, as these symptoms of intoxication decrease and the fluctuations of temperature increase correspondingly, there may be developed a certain degree of tolerance. On the other hand, as shown in animals 16 and 17, there may be an increasing resistance to the hematin from the start as the toxic symptoms as well as the temperature decrease proportionally.

This subject of acquired tolerance has been taken up largely to emphasize the importance to be attached to results obtained from properly adjusted initial doses of hematin, but also to explain the apparent discrepancies in the results from any series of hematin injections. It is the initial injection, with but few exceptions, that gives the maximum temperature reaction obtainable with a given dose of hematin until the series of injections has been extended to such a degree as to permit of the acquirement of a tolerance in highly susceptible animals or to cause a break in the early acquired tolerance of more resistant animals. When such conditions supervene, the temperature reaction may again increase and show an even greater response than with the initial injection (table I, animals 9 and 18).

SUMMARY.

The paroxysm of hematin intoxication in the rabbit undoubtedly presents many features of striking similarity to the paroxysm of human malaria; still one must hesitate to apply such results unreservedly in an attempt to identify the causative agent of the malarial paroxysm. When, in addition to the character of the paroxysm, we consider the sequence of events in the two instances, the analogy becomes so close that it seems impossible to regard the matter as a mere coincidence. The injection of hematin, especially in fractional doses, is in a measure comparable to the liberation of hematin into the human circulation by the malarial parasite. In these experiments, both solution and finely divided suspensions of hematin have been found equally effective in eliciting the phenomena of the paroxysm, and while it seems possible that a portion of the malarial pigment might be dissolved in the alkaline human serum, such an assumption is probably not essential.

It might be objected that the toxic action of foreign hematin thus injected into the circulation would probably be greater than that of hematin derived from an animal's own blood, but as far as I have been able to determine, this objection does not seem valid, as rabbit hematin, dog hematin, and ox hematin

TABLE I.—*Summary of Experimental Data.*

No. of Animal; Weight in Kilos.	Date of Injection.	Sodium Bicarbonate Salt Solution in c.c.	Hematin Solution in c.c.	Hematin per Kilo of Body Weight in mg.	Temperature (F.) at Time of Injection.	Elevation of Temperature with Sodium Bicarbonate Salt Solution.	Elevation of Temperature with Hematin.	Time in Hours to Fastigium.	Temperature 3 hours after Injection.	Remarks.
No. 1. Weight, 2.49.	Jan. 27, 1911	5.0			102.3	1.1		2	102.6	Rabbit hematin in all injections.
	Jan. 30, 1911		5.0	3.0	102.5		2.5	3	105.0	Highest temperature on secondary rise.
	Jan. 31, 1911		10.0	6.0	101.8		2.2	1½	102.8	
	Feb. 1, 1911		5.0	3.0	103.0		1.4	1½	103.0	
	Feb. 2, 1911		20.0	12.0	103.0		0.0		96.4	In two doses, 5 minutes apart. Died 3 hours after injection.
No. 2. Weight, 2.78.	Feb. 1, 1911	10.0			102.8	1.8		2½	104.3	
	Feb. 2, 1911	10.0			102.2	1.8		1½	103.0	Rabbit hematin.
	Feb. 3, 1911	23.0			102.1	2.5		1	102.8	
	Feb. 7, 1911		5.0	2.6	102.9		3.1	1¼	106.0	Initial rise to 106 degrees with fall to 105.3 degrees F. and second rise.
	Feb. 8, 1911		2.5	1.3	102.6		1.2	1	103.0	
	Feb. 9, 1911		7.5	3.9	102.5		2.6	1¼	104.0	
	Feb. 11, 1911		7.5	3.9	102.4		3.0	1¼	103.9	
	Feb. 15, 1911		15.0	7.8	102.3		4.0	1¼	106.1	
	Feb. 16, 1911		20.0	10.4	102.8		3.3	1¼	104.9	
No. 3. Weight, 2.9.	Feb. 8, 1911		2.5		102.7					2.5 c.c. thick suspension of hematin in 0.85 per cent. salt solution. Died instantly.
No. 4. Weight, 2.65.	Feb. 8, 1911	10.0			102.6	1.4		1½	102.8	
	Feb. 9, 1911		7.5	4.2	102.2		2.6	1¼	104.6	Rabbit hematin.
	Feb. 11, 1911		7.5	4.2	102.3		2.8	1¼	103.8	
	Feb. 15, 1911		10.0	5.7	102.4		2.5	1¼	104.8	

No. of Animal; Weight in Kilos.	Date of Injection.	Sodium Bicarbonate Salt Solution in c.c.	Hematin Solution in c.c.	Hematin per Kilo of Body Weight in mg.	Temperature (F.) at Time of Injection.	Elevation of Temperature with Sodium Bicarbonate Salt Solution.	Elevation of Temperature with Hematin.	Time in Hours to Fastigium.	Temperature 3 hours after Injection.	REMARKS.
No. 4. Weight, 2.65.	Feb. 16, 1911		15.0	8.4	101.6		2.1	3	103.7	Temperature dropped to 100.7 degrees F., then rose very slowly.
No. 5. Weight, 2.85.	May 1, 1911	7.0			101.8	1.3		1½	102.2	
	May 2, 1911		7.0	5.0	102.0		3.6	1½	105.0	Dog hematin.
	May 3, 1911		7.0	5.0	102.3		3.2	1¼	104.7	
No. 6. Weight, 2.57.	May 1, 1911	8.0			102.4	1.6		1½	103.0	
	May 2, 1911	10.0			101.8	1.2		1½	102.2	Other manifestations very slight.
	May 3, 1911	15.0			102.0	1.7		1¼	103.3	
	May 4, 1911	20.0			102.1	2.1		1½	103.5	
No. 7. Weight, 2.53.	May 1, 1911	8.0			101.6	1.5		2	102.0	
	May 2, 1911		8.0	4.7	101.2		3.7	1¼	104.0	Rabbit hematin.
	May 3, 1911		8.0	6.3	101.3		3.1	1¼	103.6	Dog hematin.
No. 8. Weight, 1.85.	Oct. 18, 1911	6.0			102.1	1.4		1½	102.8	Hematin solution 5 mos. old, same as that used in No. 7, injection 3.
	Oct. 20, 1911		6.0	10.0	102.3		1.8	1½	103.0	
No. 9. Weight, 2.05.	Oct. 20, 1911	12.0			102.5	2.0		1½	102.7	
	Oct. 23, 1911		12.0	12.0	102.3		3.3	1	103.4	Ox hematin in all injections
	Oct. 25, 1911		12.0	12.0	102.5		2.7	1¼	102.7	
	Oct. 26, 1911		12.0	12.0	103.6		2.0	¾	103.0	An afternoon experiment.
	Oct. 27, 1911		12.0	12.0	102.1		3.7	1	103.1	Temperature back to 103.6
	Nov. 1, 1911		12.0	12.0	102.1		4.1	1¼	103.4	degrees in 1½ hours.

No. of Animal; Weight in Kilos.	Date of Injection.	Sodium Bicarbonate Salt Solution in c.c.	Hematin Solution in c.c.	Hematin per Kilo of Body Weight in mg.	Temperature (F.) at Time of Injection.	Elevation of Temperature with Sodium Bicarbonate Salt Solution.	Elevation of Temperature with Hematin.	Time in Hours to Fastigium.	Temperature 3 hours after Injection.	Remarks.
No. 9. Weight, 2.05.	Nov. 3, 1911		12.0	12.0	101.8		4.3	1½	——	
	Nov. 6, 1911		18.0	18.0	101.5		4.9	1	103.5	Given in two doses 5 minutes apart.
No. 10. Weight, 1.85.	Oct. 25, 1911		12.0	20.0	102.6		0.8		103.0	Hematin solution 5½ mos. old, same as No 7 injection 3,and No. 8, injection 2.
	Oct. 27, 1911		12.0	20.0	102.2		1.5		102.8	
No. 11. Weight, 2.0.	Oct. 27, 1911		5.0	7.5	102.6		0.6	1	102.5	Hematin solution, same as No. 10.
	Nov. 3, 1911	12.0			101.6	1.3		1½	101.6	
	Nov. 6, 1911	18.0			101.0	2.4		2	102.2	Ox hematin in all other injections.
	Nov. 8, 1911		6.0	6.0	101.4		2.6	1	102.8	
	Nov. 10, 1911		12.0	12.0	100.4		3.0	1¾	102.8	
	Nov. 13, 1911		18.0	18.0	100.3		3.9	3	104.2	
	Nov. 15, 1911		10.0	20.0	100.5		4.5	1½	103.0	
	Nov. 17, 1911		8.0	16.0	100.8		3.2	1¼	103.2	
No. 12. Weight, 2.0.	Nov. 10, 1911		15.0	15.0	101.2		3.2	1½	103.9	Ox hematin.
	Nov. 13, 1911		18.0	18.0	101.3		4.0	1½	105.0	
	Nov. 15, 1911		10.0	20.0	101.0		3.3	1	102.9	
	Nov. 17, 1911		8.0	16.0	101.7		3.1	1¾	104.0	
	Nov. 20, 1911		10.0	20.0	102.5		1.9	1½	103.3	In two doses 30 minutes apart. Initial rise checked by second dose.
	Nov. 22, 1911		5.0	10.0	101.4		3.4	1¼	103.4	Apparently about optimum dose.
	Nov. 24, 1911		4.0	8.0	101.5		4.2	1¼	104.0	
	Nov. 27, 1911		8.0	16.0	101.4		3.0	1½	103.1	

No. of Animal; Weight in Kilos.	Date of Injection.	Sodium Bicarbonate Salt Solution in c.c.	Hematin Solution in c.c.	Hematin per Kilo of Body Weight in mg.	Temperature (F.) at Time of Injection.	Elevation of Temperature with Sodium Bicarbonate Salt Solution.	Elevation of Temperature with Hematin.	Time in Hours to Fastigium.	Temperature 3 hours after Injection.	Remarks.
No. 13. Weight, 2.15.	Nov. 22, 1911	5.0			102.2	0.4		1	101.8	Ox hematin.
	Nov. 24, 1911		4.3	10.0	102.0		1.5	1	102.2	Single dose.
	Nov. 27, 1911		4.3	10.0	102.2		3.3	1¼	102.5	In 2 doses 30 minutes apart
	Nov. 29, 1911	4.3			102.2	1.4		1¾	102.7	In 2 doses 30 minutes apart
	Dec. 4, 1911	4.3			101.6	1.4		2½	102.8	In 2 doses 30 minutes apart
	Dec. 6, 1911		4.3	10.0	101.8		3.0	1¼	103.6	In 2 doses 30 minutes apart
	Dec. 8, 1911		2.1	5.0	101.7		2.1	1½	102.6	In 2 doses 30 minutes apart
	Dec. 11, 1911		10.0	23.0	101.5		2.9	1¼	103.8	In 2 doses 30 minutes apart
	Dec. 13, 1911		10.0	23.0	102.1		2.6	1	103.0	Single dose.
	Dec. 15, 1911		12.0	28.0	101.5		3.5	1	103.5	Single dose.
	Dec. 18, 1911		12.0	28.0	101.4		4.3	1¼	104.4	Given in 2 doses 30 minutes apart.
No. 14. Weight, 2.25.	Dec. 6, 1911	4.5			100.7	1.9		2¼	102.2	Ox hematin. Given in 2 doses 30 minutes apart.
	Dec. 8, 1911	2.2			100.4	1.6		2	——	Given in 2 doses 30 minutes apart.
	Dec. 11, 1911		2.2	5.0	101.0		3.2	1¾	103.4	Given in 2 doses 30 minutes apart.
	Dec. 13, 1911		3.3	7.5	101.0		3.4	1¾	103.6	Given in 3 doses 30 minutes apart.
	Dec. 15, 1911		4.5	10.0	101.5		2.6	1½	103.0	Given in 2 doses 30 minutes apart. Over-intoxication.
	Dec. 18, 1911		6.6	15.0	101.7		2.8	1½	104.5	Single dose. Over intoxication.

No. of Animal; Weight in Kilos.	Date of Injection.	Sodium Bicarbonate Salt Solution in c.c.	Hematin Solution in c.c.	Hematin per Kilo of Body Weight in mg.	Temperature (F.) at Time of Injection.	Elevation of Temperature with Sodium Bicarbonate Salt Solution.	Elevation of Temperature with Hematin.	Time in Hours to Fastigium.	Temperature 3 hours after Injection.	REMARKS.
No. 15.	Jan. 12, 1912	3.2			100.6	1.5		1½	100.6	
Weight,	Jan. 16, 1912		3.2	10.0	99.8		3.2	1½	102.5	Ox hematin.
1.6.	Jan. 17, 1912		3.2	10.0	100.1		3.4	1½	102.3	
	Jan. 18, 1912		3.2	10.0	101.0		3.0	1	101.8	
	Jan. 19, 1912		3.2	10.0	101.2		2.5	1	102.6	
	Jan. 20, 1912		3.2	10.0	101.0		2.4	1½	101.9	
	Jan. 21, 1912									Another injection here without a record of temperature.
	Jan. 22, 1912		3.2	10.0	101.6		1.5	1½	102.0	
	Jan. 23, 1912		3.2	10.0	101.5		1.2	2½	102.7	Initial fall in temperature.
	Jan. 24, 1912		3.2	10.0	101.5		2.7	1	103.3	
	Jan. 25, 1912		3.2	10.0	101.8		3.2	1	104.0	
No. 16.	Jan. 12, 1912	3.3			101.1	2.7		1½	102.3	
Weight,	Jan. 16, 1912		3.3	10.0	100.6		3.9	1	104.4	Ox hematin.
1.65.	Jan. 17, 1912		3.3	10.0	101.8		2.8	1	102.9	
	Jan. 18, 1912		3.3	10.0	102.1		3.1	1	101.8	
	Jan. 19, 1912		3.3	10.0	102.0		2.9	1½	103.3	
	Jan. 20, 1912		3.3	10.0	102.5		3.2	1½	103.0	
	Jan. 21, 1912									Injection here with no record.
	Jan. 22, 1912		3.3	10.0	102.0		3.0	1½	103.1	
	Jan. 23, 1912		3.3	10.0	102.1		2.6	1½	103.0	
	Jan. 24, 1912		3.3	10.0	102.3		2.4	1	——	Leg broken by accident. Discontinued.

No. of Animal; Weight in Kilos.	Date of Injection.	Sodium Bicarbonate Salt Solution in c.c.	Hematin Solution in c.c.	Hematin per Kilo of Body Weight in mg.	Temperature (F.) at Time of Injection.	Elevation of Temperature with Sodium Bicarbonate Salt Solution.	Elevation of Temperature with Hematin.	Time in Hours to Fastigium.	Temperature 3 hours after Injection.	Remarks.
No. 17. Weight, 1.79.	Jan. 12, 1912	5.4			101.2	2.5		1½	103.2	Ox hematin.
	Jan. 16, 1912		5.4	15.0	101.3		4.0	3	105.3	Temperature reached 105 degrees F. in 1 hour.
	Jan. 17, 1912		5.4	15.0	101.8		2.2	1	102.7	
	Jan. 18, 1912		5.4	15.0	101.5		3.6	1	102.6	
	Jan. 19, 1912		5.4	15.0	102.0		2.6	1½	103.3	
	Jan. 20, 1912		5.4	15.0	102.0		2.6	1½	103.3	
	Jan. 21, 1912									Injection here with no record.
	Jan. 22, 1912		5.4	15.0	102.2		2.8	1½	103.2	
	Jan. 23, 1912		5.4	15.0	102.1		2.9	1½	103.3	
	Jan. 24, 1912		5.4	15.0	102.6		2.8	1	103.3	
	Jan. 25, 1912		5.4	15.0	102.6		2.6	1	103.1	
No. 18. Weight, 1.84.	Jan. 12, 1912	5.5			101.5	2.6		2	103.2	
	Jan. 16, 1912		5.5	15.0	101.6		3.4	3	105.0	Ox hematin.
	Jan. 17, 1912		5.5	15.0	102.0		2.8	1½	103.5	
	Jan. 18, 1912		5.5	15.0	101.9		2.5	1	103.6	
	Jan. 19, 1912		5.5	15.0	102.3		2.6	1½	103.8	
	Jan. 20, 1912		5.5	15.0	101.5		3.4	1½	103.7	
	Jan. 21, 1912									Injection here with no record.
	Jan. 22, 1912		5.5	15.0	101.9		3.8	1	103.4	
	Jan. 23, 1912		5.5	15.0	102.2		2.8	1½	104.7	
	Jan. 24, 1912		5.5	15.0	102.5		3.6	1	103.7	
	Jan. 25, 1912		5.5	15.0	102.7		3.3	1	104.6	

No. of Animal; Weight in Kilos.	Date of Injection.	Sodium Bicarbonate Salt Solution in c.c.	Hematin Solution in c.c.	Hematin per Kilo of Body Weight in mg.	Temperature (F.) at Time of Injection.	Elevation of Temperature with Sodium Bicarbonate Salt Solution.	Elevation of Temperature with Hematin.	Time in Hours to Fastigium.	Temperature 3 hours after Injection.	Remarks.
No. 15.	Jan. 12, 1912	3.2			100.6	1.5		1½	100.6	
Weight,	Jan. 16, 1912		3.2	10.0	99.8		3.2	1½	102.5	Ox hematin.
1.6.	Jan. 17, 1912		3.2	10.0	100.1		3.4	1½	102.3	
	Jan. 18, 1912		3.2	10.0	101.0		3.0	1	101.8	
	Jan. 19, 1912		3.2	10.0	101.2		2.5	1	102.6	
	Jan. 20, 1912		3.2	10.0	101.0		2.4	1½	101.9	
	Jan. 21, 1912									Another injection here without a record of temperature.
	Jan. 22, 1912		3.2	10.0	101.6		1.5	1½	102.0	
	Jan. 23, 1912		3.2	10.0	101.5		1.2	2½	102.7	Initial fall in temperature.
	Jan. 24, 1912		3.2	10.0	101.5		2.7	1	103.3	
	Jan. 25, 1912		3.2	10.0	101.8		3.2	1	104.0	
No. 16.	Jan. 12, 1912	3.3			101.1	2.7		1½	102.3	
Weight,	Jan. 16, 1912		3.3	10.0	100.6		3.9	1	104.4	Ox hematin.
1.65.	Jan. 17, 1912		3.3	10.0	101.8		2.8	1	102.9	
	Jan. 18, 1912		3.3	10.0	102.1		3.1	1	101.8	
	Jan. 19, 1912		3.3	10.0	102.0		2.9	1½	103.3	
	Jan. 20, 1912		3.3	10.0	102.5		3.2	1½	103.0	
	Jan. 21, 1912									Injection here with no record.
	Jan. 22, 1912		3.3	10.0	102.0		3.0	1½	103.1	
	Jan. 23, 1912		3.3	10.0	102.1		2.6	1½	103.0	
	Jan. 24, 1912		3.3	10.0	102.3		2.4	1	——	Leg broken by accident. Discontinued.

No. of Animal; Weight in Kilos.	Date of Injection.	Sodium Bicarbonate Salt Solution in c.c.	Hematin Solution in c.c.	Hematin per Kilo of Body Weight in mg.	Temperature (F.) at Time of Injection.	Elevation of Temperature with Sodium Bicarbonate Salt Solution.	Elevation of Temperature with Hematin.	Time in Hours to Fastigium.	Temperature 3 hours after Injection.	Remarks.
No. 17. Weight, 1.79.	Jan. 12, 1912	5.4			101.2	2.5		1½	103.2	Ox hematin.
	Jan. 16, 1912		5.4	15.0	101.3		4.0	3	105.3	Temperature reached 105 degrees F. in 1 hour.
	Jan. 17, 1912		5.4	15.0	101.8		2.2	1	102.7	
	Jan. 18, 1912		5.4	15.0	101.5		3.6	1	102.6	
	Jan. 19, 1912		5.4	15.0	102.0		2.6	1½	103.3	
	Jan. 20, 1912		5.4	15.0	102.0		2.6	1½	103.3	
	Jan. 21, 1912									Injection here with no record.
	Jan. 22, 1912		5.4	15.0	102.2		2.8	1½	103.2	
	Jan. 23, 1912		5.4	15.0	102.1		2.9	1½	103.3	
	Jan. 24, 1912		5.4	15.0	102.6		2.8	1	103.3	
	Jan. 25, 1912		5.4	15.0	102.6		2.6	1	103.1	
No. 18. Weight, 1.84.	Jan. 12, 1912	5.5			101.5	2.6		2	103.2	
	Jan. 16, 1912		5.5	15.0	101.6		3.4	3	105.0	Ox hematin.
	Jan. 17, 1912		5.5	15.0	102.0		2.8	1½	103.5	
	Jan. 18, 1912		5.5	15.0	101.9		2.5	1	103.6	
	Jan. 19, 1912		5.5	15.0	102.3		2.6	1½	103.8	
	Jan. 20, 1912		5.5	15.0	101.5		3.4	1½	103.7	
	Jan. 21, 1912									Injection here with no record.
	Jan. 22, 1912		5.5	15.0	101.9		3.8	1	103.4	
	Jan. 23, 1912		5.5	15.0	102.2		2.8	1½	104.7	
	Jan. 24, 1912		5.5	15.0	102.5		3.6	1	103.7	
	Jan. 25, 1912		5.5	15.0	102.7		3.3	1	104.6	

produce in the rabbit effects that are alike in both character and degree.

The dose of hematin remains as the one factor to which it is possible to attach some degree of uncertainty, but even here the author feels that the range of experimental conditions has been kept within the bounds of legitimate analogy with conditions existing in the human subject of malarial infection.

Finally, the most conservative estimate of the value of such experiments points strongly to the fact that we have at least a potentially toxic substance in the pigment hematin as liberated by the malarial parasite into the circulation of the human host.

There is also abundant evidence to show that the action of hematin is not confined to the paroxysmal phenomena of malaria, but that other features of the disease may find their explanation in the action of this pigment. For the present, however, it seems advisable to confine the discussion to this one phase of the question.

CONCLUSIONS.

1. Alkaline hematin in doses commensurate with the amounts of hematin liberated in the human circulation by the segmentation of the malarial parasite, produces, when injected intravenously into the rabbit, a paroxysm which is characterized by a short prodromal stage, a stage of chill and rising temperature, and a hot stage. In their details the phases of this paroxysm are practically identical with the corresponding ones in the paroxysm of human malaria.

2. The phenomena in human beings infected with malaria are, at least in part, directly referable to the toxic action of this malarial pigment.

UNIVERSITY OF NORTH CAROLINA.

THE PAST, PRESENT, AND FUTURE OF THE NAVAL STORES INDUSTRY.*

By Chas. H. Herty.

The limited use of the oleoresinous exudate of pine trees dates back many centuries, but the real beginning of an industry on a large scale is closely associated with the discovery of the vast pine forests which extend along the southeastern and southern coasts of the United States from North Carolina to Texas.

These forests lie chiefly in the coastal plain and in the slightly hilly country between the Piedmont plateau and the coastal plain, a strip varying in width from one hundred to two hundred miles and characterized by a sandy soil, covered for the most part with "wire-grass," this furnishing a beautiful carpet of green in spring and summer, but making a serious fire risk in winter. The longleaf pine readily sheds its lower limbs, especially in close stands, so that the forests are remarkably open and free from that undergrowth, which, in the northwest, leads to such destructive forest fires.

The early settlers in eastern North Carolina began the exploitation of their forests of longleaf pine for the purpose of providing tar and pitch for use in the construction of wooden ships, and gradually extended their operations to the collection of crude turpentine which was shipped to northern cities or England for distillation. The forests covered the entire territory and, as clearings for farms were needed, destructive methods of operation were welcomed and encouraged.

At the same time limited operations were being conducted upon the maritime pine in southwestern France between Bordeaux and Bayonne. To receive the crude turpentine the French made use of a hole dug in the sand at the base of the tree. The oleoresin flowing from the wound on the trunk above was collected in these holes. Necessarily by this method much of the material was wasted and rendered impure.

* Reprinted from Original Communications, Eighth International Congress of Applied Chemistry. Vol. XII, p. 101.

AMERICAN METHOD OF COLLECTION.

In North Carolina the method of collection was improved, or thought to be improved, by cutting a large opening, the "box," in the base of the tree. Into this box the crude turpentine flowed and was collected at regular intervals. The conservative character of the men engaged in this industry led to the continuance of this wasteful and destructive method of "boxing" until the very recent past.

Briefly, the method of operating so long in use in the United States is as follows: In the winter the laborers are engaged in cutting "boxes." Each box is then "cornered," a wide chip being removed from each half of the box to provide a surface suitable for directing the flow of crude turpentine to the box. Meanwhile, other laborers are employed in clearing all combustible material from around each tree, "raking." Ground fires are then started to consume the dead wire grass, chips, etc. With the opening of spring "chipping" begins. This consists in scarifying each week the trunk of the tree above the "cornered" surface by means of a "hack," a U shaped steel tool set in a wooden handle. Attached to this handle is a heavy iron weight to give momentum to the free arm swing used in chipping. After four or five weeks the "boxes" average a good filling and the crude turpentine, "dip," is then transferred to buckets by flat, iron paddles, and from the buckets it is collected in barrels conveniently placed in the woods. In the fall, at the end of the chipping season, the hardened oleoresin, which which has gradually collected during the chipping season on the scarified surface of the tree, is removed by scraping, giving thus the name "scrape" to this product, which is sold as "Gum Thus," or distilled. In the following winter the trees are again raked and the grass fired, and in the spring chipping is resumed at the point on the trunk of each tree where it ceased the previous year. This cycle is usually continued from three to four years, although in early days it was often continued ten or twelve years, the scarified surface extending high on the trunks. Necessarily the yield from such high chipping was largely decreased, owing to the increased distance of flow to the receptacle.

In the early days of the North Carolina industry, no effort was made to distill the product, but gradually it became clear that it would be better to separate the crude turpentine into spirits of turpentine and rosin by distillation in the woods. For this purpose iron stills were used at first, but results were unsatisfactory until the introduction of copper stills, which were less liable to crack and could be heated with greater uniformity and better control.

The industry now began to grow rapidly and before many years it was found that the supply of available timber in North Carolina was rapidly decreasing. This led many of the operators to transfer their operations to the virgin forests of the adjoining state of South Carolina, where the same destructive methods were applied by the same men or their descendants. In this way, and for these reasons, the center of the industry has gradually moved southward and then westward as evidenced by the relative prominence of the ports for exports of the products; first Wilmington, N. C., then Charleston, S. C., then Savannah, Ga., and now the latter, together with Jacksonville, Fla., and the gulf ports, Tampa, Fla., Pensacola, Fla., Mobile, Ala., Gulfport, Miss., New Orleans, La., and others.

FRENCH IMPROVEMENTS.

The steady growth of the American industry received a serious check during the Civil War. The consequent scarcity of the products was accompanied by an abnormal increase in their value. This enhanced valuation led Hugues, a Frenchman, to propose a less wasteful method for the French forests than the hole dug in the sand. He proposed as a substitute a clay pot, holding about one pint. The pot was supported on its bottom by a large nail driven into the tree and on one side of its upper rim by a strip of sheet zinc, approximately 2″ x 4″, slightly curved and driven into a correspondingly upwardly inclined cut in the wood. This spout served to direct the oleoresin into the pot. At first his proposition was scoffed at and the peasants amused themselves by breaking the little pots. It is a pitiful

commentary that Hugues died in poverty; but his ideas lived and gradually became adopted in France.

AMERICAN IMPROVEMENTS.

As the knowledge of the new method in France spread to this country, numerous efforts were made to apply similar forms of apparatus to the American system of chipping, but for many years such efforts failed. No less than fifteen patents were issued in the United States on this subject, but no one of them proved a commercial success.

Eleven years ago the writer began a series of field experiments on a small scale in the turpentine forests of South Georgia. One feature of these experiments was the use of a modification of the Hugues system, consisting of two separate metallic gutters, inserted in upwardly inclined cuts in the tree, along which the oleoresin flows. The upper and shorter gutter is separated at its lower end about one inch from the lower gutter and empties into it. The lower gutter extends from two to three inches beyond the center of the angular scarified surface formed in chipping, and serves as a spout to convey the oleoresin to a cup suspended from a nail just below the end of the gutter. These cups are made either of well burned clay or galvanized iron, and have a capacity of one quart.

Attracted by the promising character of these preliminary experiments, the U. S. Bureau of Forestry began a series of field tests of the apparatus on a large scale, the work being under the immediate supervision of the writer. Before the end of the first season of testing it was evident that the apparatus was a practical success, and the results attained, both as to quantity and quality of oleoresin, justified the hope of immediate commercial introduction of the system. But the habits of long years made difficult the adoption of such an innovation. This ultra-conservatism was slowly overcome and the adoption of the new system spread rapidly. Only a few more years will be required to witness the complete replacement of the "box" by the "cup" system in American forests. A detailed account

of these experiments is given in Bulletin No. 40 and Circular No. 34 of the U. S. Bureau of Forestry.

With the main points at issue settled, namely—improved yields both in quantity and quality of the products and preservation of the trees, other forms of apparatus were devised to meet the objections of some of the operators to certain points in the cup and gutter system. Many of these have never proved practical, but some have been introduced on a considerable commercial scale.

The successful outcome of the experiments on the relative yields from the "box" and the "cup" system led the United States Forest Service to further experiments in more conservative treatment of the trees in chipping. Comparative studies were made of the yield from deep and shallow chipping and the latter found to give the greater yield during a period of four years of operation. Other experiments showed that a less rapid rate of ascent of the trunk also gave larger yields, and experiments combining these several modifications of present practices showed a largely increased yield. A final set of experiments pointed clearly the rational way to a perpetuation of the naval stores industry in America. The details of this investigation are given in Bulletin No. 90 of the United States Forest Service.

DISTILLATION.

In the matter of distillation, only slight advances have been made in America. The uniform process consists in the use of a large copper kettle and condensing worm. The charge for a distillation averages nine to ten barrels of crude turpentine. The kettle is heated by free flame and during the distillation a small stream of hot water from the top of the condenser tub is admitted through an opening in the upper part of the kettle, thus facilitating the removal of the volatile oil. The condensed spirits of turpentine and water separate in the receiver, owing to difference in specific gravity, and the lighter spirits of turpentine is transferred to oak barrels, well coated with glue on the inside. No effort is made to redistill this product, and it always comes upon the market contaminated by a small amount

of resin carried over mechanically during distillation. After most of the volatile oil has passed off, the still cap is removed, excess water in the kettle boiled off, and the molten rosin drawn off through a tap in the bottom of the kettle onto a coarse wire filter, then through a second filter of fine mesh wire overlaid with cotton batting. The molten rosin is then dipped into wooden barrels luted with clay and solidifies on cooling. In this condition it is shipped to market.

The usual method of controlling the distillation is by the sound heard at the mouth of the condenser worm. Within the past three years a number of American operators have substituted for this method that of thermometer control with very excellent results.

In France, much more progress has been made in the art of distillation. Among the French distilleries there are three distinct types: first, a system closely resembling the American; second, distillation solely by steam in steam jacketed vessels; and third, a mixed system in which there is direct contact of fire with the kettle during the first stage of the distillation, then replacement of this by mixed injection of steam and hot water. By this means, a constant temperature is maintained, enabling the complete removal of all spirits of turpentine without danger of scorching the rosin.

It can be readily understood that in France, under proper methods of forestry, with conservative tapping of the trees and provision for systematic reforestration, a distillery can look forward to a permanent supply of raw material. Hence there is justification for the more costly plants and more efficient methods of distillation; but in America, where under past methods the industry shifts so rapidly, so great an outlay of capital for this purpose would not be justified. There is no doubt that with an excellent "stiller" very good results can be obtained under the American system, but the personal element of the stiller enters into the question and this could be easily avoided without any great outlay of capital by adopting the French system of mixed injection.

Quite recently M. Castets has erected near Dax, France, a

distillery which combines the features of continuous distillation in a partial vacuum and condensation by pressure of the waste spirits of turpentine vapors from the ordinary condenser in a second condenser attached to the first, thus increasing notably the yield of volatile oil and improving the quality of the rosin.

THE INDUSTRY IN OTHER COUNTRIES.

There is no need of any especial consideration of the Spanish industry, which has developed considerably during the past decade. The operations are essentially the same as the French, and the same species of pine, *Pinus Maritima,* is exploited.

In Austria the industry is more limited and is even more destructive than by the old American system; a "box" being cut in the base of the tree, *Pinus Laricio,* and the trunk of the tree scarified for at least fifty per cent. of its circumference, the oleoresin being directed towards the center of the scarified surface by thin wooden strips inserted in downward cuts in the tree.

In Russia the chief tree exploited is *Pinus Sylvestris.* Climatic conditions do not admit of the usual process of collecting the crude turpentine at regular intervals. Instead, the trees are scarified in the spring over a space about three feet high and almost encircling the tree. During the year a mass of hardened rosin collects on this surface. In the winter it is scraped from the tree and distilled for its volatile oil and resin. This process is repeated for five years. The tree is then felled and the rosinous portion of the tree subjected to destructive distillation. In other districts no effort is made to collect the rosin from the trees annually, but this is allowed to remain until the end of the fifth year of scarification. The tree is then felled and that part containing the rosin distilled first at a low temperature to obtain the volatile oil, then at a more elevated temperature to obtain tar and charcoal by destructive distillation of the wood.

The spirits of turpentine from Germany, Sweden, and Finland, seems to be a product solely of the destructive distillation of resinous wood.

The production of naval stores in India and other tropical countries is at present on too small a commercial scale to call for any detailed discussion here.

WOOD SPIRITS OF TURPENTINE.

Among the various departments of the naval stores industry in America none has had a more varied and interesting career than that of the production of "wood spirits of turpentine" by destructive distillation of resinous wood. Years ago considerable capital was invested in plants for utilizing the by-products formed during the destructive distillation of "fat lightwood." None of the plants were commercially successful and for awhile nothing was heard of the industry. But with the increase in price of spirits of turpentine resulting from the formation of the Turpentine Operators Association in 1902 a fresh impetus was given to the "wood spirits of turpentine" industry. At first somewhat crude methods of destructive distillation were advocated, and as the promoters of this industry appealed largely to local interest in having stumps for distillation removed from fields suitable for cultivation, a double impetus was received. Much enthusiasm was aroused, and a number of plants constructed. But the industry received a serious blow in the refusal of the varnish makers to use the impure "wood spirits of turpentine" manufactured, by the failure to find a market for many of the heavier oils and the coke, and by the destruction by fire of many of the improperly constructed plants.

The price of spirits of turpentine continued to rise and led to the development of the steam extraction process for manufacture of wood spirits of turpentine. After thorough grinding, the wood is treated in iron retorts with steam, and the volatile oil distilled, no effort being made to obtain any other product. By one redistillation of the product a very high grade spirits of turpentine is obtained, equal, if not superior, to that from the living tree. Unfortunately, the yield is not sufficiently large to make the process remunerative.

Quite a different process is employed by those plants which

utilize a bath of molten rosin for removal of the spirits of turpentine from the wood, with subsequent distillation of the volatile oil from this bath. Such plants seem to have met with a fair measure of success.

More recently extraction processes have been developed which employ low boiling petroleum products as the extractive. Such plants recover both the spirits of turpentine and the rosin from the ground wood, and have a great advantage in the present very high value of rosin. These plants are also utilizing the refuse from the straining of rosin at the distilleries in the woods, a product formerly burned on the waste piles, but now bringing nineteen dollars per ton. This method is adding a considerable amount to the annual output of rosin.

The most recent development is a plant for destructive distillation of wood in retorts heated by jackets filled with high boiling petroleum fractions. By this means a fire risk is practically completely eliminated and the results indicate that by means of the complete and ready temperature control of the oil jacket larger yields of better products can be obtained.

ANNUAL PRODUCTION OF NAVAL STORES.

No subject connected with the naval stores industry admits of so little accuracy of statement as does that of statistics on the total annual production. The most careful estimates are at best only approximations. This is unfortunate, for in the past it has frequently led to speculative manipulations of the market and the temporary establishment of values which had no legitimate basis depending on supply and demand.

The following table of annual production is given therefore, as an approximation only, but it is believed to be a reasonably accurate approximation:

	Spirits of Turpentine (barrels 52 gallons)	Rosin (barrels 500 lbs.)
America	600,000	2,100,000
France	100,000	350,000
Spain	25,000	87,500
Austria	3,000	10,500
Other countries	50,000(?)	(?)
Total estimated production	778,000	2,548,000

PRODUCTION OF CRUDE TURPENTINE PER TREE.

Here again definite figures are difficult to give, for there is no reliable information concerning the number of trees in operation. Furthermore, there is often very wide variation in the producing power of adjacent trees of the same species, size, and crown. But from the data in the publications of the United States Forest Service, an average American pine, worked under the cup system, will produce, during four years of operation, an annual average of ten pounds of crude turpentine and two and a half pounds of "scrape," the proportionate yield being considerably greater during the first and second than during the third and fourth years of operation.

The average daily flow of crude turpentine during one week from a freshly chipped surface on such pines is shown in the following table, the results having been obtained during the summer of 1901 on trees near Statesboro, Georgia:

	Yield per tree (grams)			Average yield (grams)	Per cent. average yield
Day	1	2	3		
1	113.0	46.5	89.0	82.8	62.9
2	22.5	7.5	16.0	15.3	11.6
3	13.5	6.5	16.0	12.0	9.1
4	9.0	5.0	17.0	7.0	5.3
5 & 6	9.0	5.0	23.0	12.3	9.3
7	1.0	2.0	4.0	2.3	1.8
Total	168.0	72.5	165.0	131.7	100.0

TSCHIRCH'S VIEWS ON RESIN FLOW

As to the seat of resin production and cause of resin flow, most valuable and important views have been advanced by Prof. A. Tschirch in his book "Die Harze und die Harzbehälter," 2nd edition. Tschirch has shown that the seat of resin production is a mucilaginous layer lining the inner walls of the resin ducts. These ducts he divides into two classes: First—primary ducts, whose resin is to be considered a true physiological product. Such ducts occur irregularly and in varying number in any pine. They play only an insignificant role as producers of commerical crude turpentine. Second—secondary resin ducts which form in large numbers in the outer layers of the new wood after a tree is wounded, both above and below the wound. Their oleoresinous exudate is, therefore, a pathological product. It is from such pathological ducts that the great bulk of crude turpentine is obtained.

The application of these views to practical problems in the turpentine forests has already yielded important and fruitful results.

FUTURE OF THE INDUSTRY

During the past few years the statement has frequently been made that from present indications the naval stores industry must cease to exist, at least as a large industry, within the next twenty years. While it is true that there are danger signals which must be heeded, such pessimistic views do not seem to be well grounded.

Certainly in France and consequently in Spain, where the same system is in operation, the industry has been placed upon a self-perpetuating basis.

In America we have been prodigal with our wealth of virgin forest.

But it must be remembered that until the last decade these forests have had a very low commercial valuation. The average price for well timbered lands in our southern states not many years ago was approximately one dollar per acre, land, timber, and all. Indeed, the popular term applied to all holders of

large tracts of such lands was "land poor," as expense of taxation, protection, etc., exceeded any hope of probable profit. This condition was largely due to lack of transportation facilities, insecurity of title, low price of naval stores and lumber, lack of knowledge of the farming value of much of the land on which these forests stood, and the belief that the forests were inexhaustible.

Now conditions have entirely changed. Railroads penetrate every portion of the territory, titles have been cleared, prices of naval stores have brought wealth to the operators, the lumbermen from Michigan, Wisconsin, and other northern states have turned from the rapidly disappearing white pine forests of the north to those of the southern yellow pine; where forests once stood farms have been developed which surpass in fertility any other portion of the southern states, and a clear knowledge has been gained that the forests are by no means inexhaustible. Furthermore, the spirit of conservation of natural resources has made itself felt in this field as well as in those of minerals, water power, etc.

The consequence of these changes has been a very rapid enhancement in the value of such holdings. And with increased valuation comes naturally the desire to protect and use conservatively. Unquestionably, the stand of virgin forest will still further diminish, for the demand for farm lands is active, the call for lumber imperative, and the danger of tropical storms along the Gulf Coast ever present. With such diminution in supply will come still further enhancement in values and still more conservative methods of operation.

So much for the present stand of virgin forest. If the situation were limited to this alone, the outlook might be considered gloomy. But it must be remembered that there are vast tracts of cut-over lands in portions of the southern states whose clay sub-soil lies so deep that the lands are not suited to agriculture. On such lands the longleaf pine, with its long tap root, prospers. Magnificent forests once covered every acre of such lands and fortunately tree planting is not required to reproduce such forests. Nature alone will again cover this territory with a

wealth of forest, provided Nature is given an opportunity; for the most superficial observer who travels through this territory will testify that where conditions have been favorable natural reproduction has brought again splendid, though small, young forests.

Against this willingness of Nature to restore this rich heritage to us, stand three agencies:

First, and of least importance, the consumption by hogs of the delicately flavored and nutritious seed of the longleaf pine. This is a real factor in certain somewhat restricted districts. The constantly spreading sentiment for "stock laws" will check this evil.

Second, and of the very greatest importance, the destructive action of the ground fires, Fig. 7, which annually sweep over the entire turpentine belt. Such fires destroy the myriads of young seedlings which can readily be seen springing up in the wire grass which surrounds them on every side. The seedling devotes the greater part of its early energies to sending down its long tap root through the deep sands rather than to strengthening its stalk above ground; hence, in most cases, it is not able to withstand the constantly recurring ground fires. The doctrinaire may rail against the evils of such firing of the woods, but from one who has lived among the turpentine camps there comes no word of reproach against the turpentine operator who "burns the woods." His all is invested on the outer surface of his trees. A serious outbreak of fire during midseason means financial ruin. The carelessness and sometimes viciousness of laborers is too serious a risk to run with a mass of dead wire grass covering every foot of his territory. Naturally he protects himself by burning this grass when he is prepared for it, after "raking season."

Where then is the hope for reforestration? In the realization of the value of the waste cut-over lands where turpentine operations cannot be carried on for lack of timber. Such lands have now but little value, but the lesson of France shows that even there a reasonable income begins from artificial reproduction within a period of twenty years and then rapidly increases.

With our warm southern climate the prospect for rich returns from such investments should be even greater than in France.

Third, the greed of man. If we are to have a self-perpetuating industry, even stock laws and the reforestration of waste lands will not avail if a practice on the part of turpentine operators during the past two years continues. The abnormally high price of spirits of turpentine two years ago led to a wild scramble for timber for increased operations. At the same time the efficiency of the cup system was just gaining wide recognition. Realizing that a tree too small to have a "box" cut in it could be worked with a cup hung upon it, the operators throughout the whole region proceeded to cup every small tree to which access could be gained. In many cases new farms were opened on old abandoned territory where natural reproduction had furnished thrifty young forests. The result was over-production of crude turpentine. The temporary benefit to the consumers in the drop in values following this over-production was dearly bought, for the price was the destruction of young forests which in time should have produced their full share of the world's need of spirits of turpentine and rosin. Common sense must and will govern in this matter. It is only necessary for the operators to realize that the yield from such saplings does not meet the cost of production, then the practice will cease.

Surely the above considerations justify an optimistic view of the future of the naval stores industry. But experiment, demonstration, statistics, and knowledge of progress made in other lands, must lead the way for the man in the woods.

UNIVERSITY OF NORTH CAROLINA.

THE RESENES OF RESINS AND OLEORESINS*

By Chas. H. Herty and W. S. Dickson

The oleoresinous exudate of pine trees, commonly called "crude turpentine," consists of a mixture of a volatile oil, acids and unsaponifiable matter. On distillation with steam the volatile oil, "spirits of turpentine," passes off; the residual resin, freed from excess of water by heating, solidifies on cooling and constitutes commercial "rosin." The name "resene" has been applied by Tschirch[1] to the non-volatile, unsaponifiable constituent of such resins and oleoresins.

[1] Tschirch, "Die Harze und die Harzbehälter," Second edition, p. 1079.

Though the composition of crude turpentine varies considerably in different specimens, an average analysis of specimens collected by the usual commercial methods would show approximately:

	Per cent.
Spirits of turpentine	20
Acids	74
Resene	6

Resenes, according to their origin, show varying physical states, some being colorless solids while many are very viscous liquids, extremely sticky and non-crystallizable. They are composed of carbon, hydrogen and oxygen, but the per cent. of oxygen is usually smaller than in the accompanying acids. Toward reagents they are very resistant, especially toward alkalies. Although containing oxygen, they show, according to Tschirch,[2] none of the usual reactions indicating the presence of hydroxyl, carboxyl, aldehyde or ketone oxygen, nor are they ethereal salts or lactones. Tschirch inclines to the view that they belong to the class of exyterpenes or oxypolyterpenes.

While much work has been done upon the volatile oils and the acids of oleoresins, little attention has been paid to the resenes, except ultimate analyses and approximate statements of the proportion present in isolated specimens studied. In connection

* Reprinted from the *Journal of Industrial and Engineering Chemistry*, Vol. IV, No. 7, July, 1912.

[2] *Loc. cit.*

with an investigation carried out in this laboratory in collaboration with the United States Forest Service, there remained a large number of specimens of resin from well identified individual trees growing in Florida. It seemed desirable, therefore, to study more closely the question of the proportions of resene in these specimens. The investigation was extended to the resins of conifers growing near this laboratory, and to specimens collected in other countries. Finally the amount of resene was determined in several oleoresins obtained in perfectly fresh condition from individual trees in Florida. These specimens were collected from the two species of pines from which crude turpentine is commercially obtained in this country, *Pinus Palustris* (Longleaf Pine), and *Pinus Hetrophylla* (Cuban or Slash Pine).

The resins were obtained by distilling the oleoresins in a current of steam slightly superheated, the temperature being raised to 140° C. toward the end of the distillation. After complete removal of the volatile oil, the residue was kept at 140° C. in the oil bath surrounding the distillation flask until all water was driven off. The molten resin was then filtered through absorbent cotton and cooled to solidification in glass or iron molds.

The determination of resene in the resins was carried out in the usual manner. The weighed specimen, about two grams, was dissolved in a considerable excess of *N*/2 alcoholic potassium hydroxide, allowed to stand at room temperature eighteen hours, diluted with water until separation of the resene began and the solution cleared by the addition of a small quantity of ninety-five per cent. alcohol. This solution was then extracted three times with petroleum ether, boiling below 40°c. The combined extracts were shaken out with fifty per cent. alcohol to remove slight amounts of dissolved potassium salts of resin acids. After drawing off the petroleum ether extract into a weighed glass evaporating dish, it was allowed to evaporate spontaneously to constant weight.

In the case of the oleoresins, after spontaneous evaporation of most of the petroleum ether, the residue was heated for five hours on a steam bath in order to remove completely the petro-

leum ether and the volatile oil. Considerable difficulty was experienced at the outset in these evaporations due to the tendency of the material to "crawl" over the rim of the vessel. This was entirely overcome by using a thin coating of vaseline on the rim of the vessel.

The following results were obtained:

TABLE I.—PER CENT. OF RESENE IN RESINS FROM DIFFERENT SPECIES

Species.	Local name.	Origin.	Per cent. resene.
Pinus Taeda	Loblolly Pine	North Carolina	4.10
" Palustris	Longleaf Pine	Florida	5.67
" Maritima	Maritime Pine	France	7.37
" Heterophylla	Cuban or Slash Pine	Florida	7.38
" Serotina	Pond Pine	Florida	7.65
" Echinata	Old Field Pine	North Carolina	8.71
" Species unknown		Central America	8.94
" Sabiniana	Digger Pine	California	9.66
" Laricio	Schwarzkiefer	Austria	14.05

In order to test the variation of the amount of resene in trees of the same species two sets of determinations were carried out on trees of different diameters. The results follow:

TABLE II.—PINUS PALUSTRIS (LONGLEAF PINE).

Tree No.	Diameter (inches).	Per cent. resene in resin.
1	7.3	5.26
2	15.0	5.95
3	21.0	9.68
4	13.0	7.45
5	8.7	5.67
6	9.0	5.45
7	13.5	6.22

TABLE III.—PINUS HETEROPHYLLA (CUBAN OR SLASH PINE).

Tree No.	Diameter (inches).	Per cent. resene in resin.
1	7.0	7.87
2	14.5	7.36
3	24.5	7.20
4	12.3	7.25
5	8.2	6.58
6	13.0	7.84
7	9.0	7.00

To determine possible variations in the per cent. of the resene in different seasons of the same year two trees were selected, one each, *Pinus Palustris,* tree No. 2, Table II, and *Pinus Heterophylla,* tree No. 2, Table III. Beginning in the early spring

the oleoresins were collected from these at regular periods of four weeks until the close of the season in the fall. From the resins prepared from these specimens the following results were obtained:

TABLE IV.

Collection No.	Per cent. resene in resin from Pinus Palustris.	Pinus Heterophylla.
1	5.31	7.36
2	5.44	7.67
3	5.95	7.23
4	6.02	8.17
5	6.09	7.38
6	6.53	7.43
7	5.24	7.77

It is scarcely probable that in the case of *Pinus Palustris* any significance is to be attached to the gradual increase in the per cent. of resene as the season advanced until the last collection.

Further determinations were made of the per cent. of resene in specimens of oleoresin collected with great care in Florida and promptly analyzed. The following results were obtained:

TABLE V.

Tree No.	Per cent resene in oleoresin of Pinus Palustris	Pinus Heterophylla
1	7.10	6.83
2	3.84	6.76
3	7.33	6.96

Finally, a specimen of "scrape" (Gum Thus) was obtained from a Longleaf pine (*Pinus Palustris*). This scrape is the hardened mass which gradually collects on the scarified surface of the tree as a result of the crystallization of the resin acids of the oleoresin. It receives its name from the fact that at the end of the season it is scraped from the surface of the trees by means of a sharp tool. It contains approximately one-half as much spirits of turpentine as the ordinary oleoresin collected from the receptacles. The resin was prepared from this scrape by distillation with steam as above. On analysis it showed 3.14 per cent. of resene.

In continuation of this work, there is now being carried out in this laboratory an investigation of the composition of the resene of *Pinus Heterophylla.*

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THE VALUE OF COMMERCIAL STARCHES FOR COTTON MILL PURPOSES.

By G. M. MacNider.

Large quantities of starch are used annually by the cotton mills in the processes of sizing and finishing. The yarn is prepared for weaving by a process known as sizing, in which it is treated with a solution of starch to give it certain properties essential to good weaving. When the cloth comes from the loom it is put through a process known as finishing to produce a certain "finish" before it is ready for the market. It is essential to good weaving that the yarn be properly sized before going to the loom and with many grades of cloth the finish produced by the starch largely determines the market price of the goods. It is therefore seen that starch plays a very important part in the manufacture of cotton goods, and hence the purchase of the kind of starch best adapted to the purpose in hand is a very important matter.

The object of sizing is to make the yarn stiffer, increase the strength and put it into proper condition for weaving. To accomplish this the size must penetrate the yarn to some extent and also form a coating on the surface of the thread, which prevents wear of the thread in the loom. The size is prepared by boiling the starch (and other ingredients) with water in an iron kettle known as the size-kettle. When the mixture has been boiled for a sufficient length of time it is run out into the size-box of the sizing machine and kept hot while the yarn is passed through it. Two systems of sizing are in use: the short chain system, or old system, in which the yarn is sized in hanks, and the long chain or slasher system in which the yarn is sized from the beam. The same results are obtained by both systems, the slasher system being faster than the short chain system. In both systems the yarn is dried as soon as it comes from the starch solution.

The object of finishing is to increase the stiffness of the cloth and produce a finish and feel on the cloth which are very import-

ant factors in marketing cotton goods. The finish mixture is prepared in a manner similar to the size mixture and is applied to the cloth while hot. When the cloth is dry it is calendered to bring out the finish. The use of a starch solution alone in these operations would make the goods too stiff and produce a harshness which is not desirable. To modify this effect many softening agents are used, such as tallow, oils, soaps, glycerine, etc. As finishing is the final operation it is very important that it should be properly carried out and the best effect obtained from the starch. If it is desired to increase the weight of the goods this can best be done in the finishing process. For this purpose the finishing mixture is made very thick, or where this would produce too much stiffness in the cloth thin boiling starches may be used to give the weight without undue stiffness.

The principal starches used in the textile industry are corn, potato, cassava, sago, and to a small extent wheat and rice. Wheat and rice starches are, however, more largely used as laundry starches.

The value of starch for cotton mill purposes depends on its property of swelling and forming a viscous solution when treated with hot water. It is well known in practice that the different starches produce different effects in sizing and finishing. One kind of starch will penetrate the goods better than another. This variation is due to a difference in the thickness of the solutions formed by the different starches when boiled with water, that is, one starch forms a more viscous solution than another. The thickness or viscosity of the solution formed by starch is the most important point to be known in determining the value of a starch for textile purposes, for on this depends the penetration of the starch solution into the yarn or cloth, and hence the stiffness which will be given to the goods when sized or finished. As the viscosity of the starch solution is such a valuable indication of the value of the starch it is very important to have a method for determining the viscosity which will give results comparable to actual practice. The following method has been devised for this purpose:

Twelve grams of the starch are weighed into a 600 cc. beaker,

300 cc. distilled water added (thus making a 4 per cent. solution) and heated with constant stirring to the boiling point and boiled for ten minutes; 200 cc. of this solution are then poured into the cup of a Scott viscosimeter, the temperature allowed to become constant, usually 94° C., and 50 cc. run out into a graduate, the time being accurately measured with a stop watch. The number of seconds required to deliver 50 cc. of the solution divided by the number of seconds required to deliver 50 cc. of boiling water gives the viscosity.[1]

It will be noticed from this that the starch solution is prepared by boiling with water as is done in sizing and finishing and the viscosity is measured at very near the boiling point of the solution, so that the figures obtained show the effect of boiling on the different starches.

The viscosities of the principal commercial starches are shown in the following table.

TABLE I.—VISCOSITIES OF COMMERCIAL STARCHES.
(12 grams starch in 300 cc. water, boiled ten minutes.)

Starch	Viscosity
Corn	3.05
Potato	14.31
Cassava	3.92
Sago	1.57
Wheat	1.25
Rice	1.00

From the above table it is seen that there is a wide variation in the viscosities of the different starches and hence a wide variation in their value for mill purposes. The viscosity of potato starch is much higher than that of any other starch, but there is also a considerable variation between the viscosities of the other starches. The importance of the viscosity will be seen more fully in the next section in showing the effect of boiling on the viscosity of starch solutions. It has been found that there is frequently considerable variation in the viscosities of different lots of the same kind of starch. It would be very advantageous to the mills for each lot of the same kind of starch to have a uniform viscosity. This would make it possible to

[1] A detail description of this method was published in the *Journal of Industrial and Engineering Chemistry*, Vol. IV, No. 6, 1912.

obtain the same results in sizing and finishing without changing the formula for each lot of starch.

In practice the starch solution is boiled from thirty minutes to one hour before being used. It is therefore very important to know the effect produced by boiling on the viscosity of the starch solution. This is shown in the following table.

TABLE II.—SHOWING THE EFFECT OF BOILING ON THE VISCOSITIES OF COMMERCIAL STARCHES.

(12 grams starch in 300 cc. water.)

Starch	Minutes Boiled	Viscosity
Corn	at boil	2.15
"	10	2.73
"	20	4.26
"	30	7.00
Potato	at boil	16.37
"	5	19.51
"	10	14.31
"	30	6.33
Cassava	at boil	9.93
"	5	4.53
"	10	3.88
"	20	3.91
"	30	4.17
Sago	at boil	1.88
"	5	1.62
"	10	1.57
"	30	1.66
Wheat	at boil	1.20
"	5	1.22
"	10	1.26
"	20	1.24
"	30	1.33
Rice	at boil	1.00
"	10	1.00
"	30	1.08

From the above table it will be seen that the viscosity of corn starch increases uniformly with the length of time of boiling. This increase is about what would be expected with the concentration of the solution when there is no change in the starch. This is a very valuable property of corn starch as compared with other starches and gives corn starch a much wider application in the textile industry than any other starch. The value of this property will be seen more clearly by comparison with potato starch.

Potato starch reaches its maximum viscosity after being boiled five minutes. From this point the viscosity decreases

rapidly with the increase in time of boiling, the concentration of the solution apparently having no effect on the viscosity. After boiling ten minutes potato starch has a viscosity slightly more than five times as great as corn starch, while after boiling thirty minutes the viscosity of potato starch is less than that of corn starch which has been boiled the same length of time. This property of potato starch of liquefying on boiling is a very important point to be considered in using this starch. In sizing the starch is boiled from thirty minutes to one hour before being used, hence, as will be seen from the table, a size mixture made of potato starch will have a viscosity less than that of a similar size made of corn starch at the time it is ready to be applied to the yarn. In other words, the potato starch size will not be as valuable for sizing as the corn starch size, but it will cost approximately twice as much as the size made from corn starch.

Cassava starch attains its maximum viscosity at the boiling point. The solution apparently has a higher viscosity shortly after complete gelatinization takes place, but no measurements were made of this as the starch is not used until it has been boiled. After reaching the boiling point the viscosity decreases uniformly with the length of time of boiling. After boiling thirty minutes there is an increase in the viscosity over that of the solution boiled twenty minutes. This increase is probably due to increase in concentration. As will be seen from the table, cassava starch behaves in a manner very similar to potato starch as regards liquefaction of the solution, but not to the same extent. Cassava starch therefore has a much broader application in sizing and finishing than potato starch.

Sago starch has a much lower viscosity than any of the starches so far considered. Like cassava starch it apparently has a higher viscosity at the time of complete gelatinization, but no measurements were made of this. The viscosity is highest at the boiling point and decreases uniformly on boiling, though not to the same extent as the other starches. After boiling thirty minutes there is a slight increase in viscosity due to the concentration of the solution. While having a consider-

able lower viscosity sago starch is quite similar to cassava starch as regards the effect of boiling on the solution.

Wheat starch shows a gradual increase in viscosity with the time of boiling, similar to corn starch, though the total increase is small, the viscosity of the thirty minute determination being only slightly higher than the determination made at the boiling point.

Rice starch has the same viscosity as water when measured under these conditions. At the end of thirty minutes boiling it shows only a very slight increase in viscosity.

The marked differences in the effect of boiling on the viscosities of the different starches is due to the fact that some starches form soluble starch products more readily than others. The data given in the preceding table shows very plainly the importance of the viscosity in determining the value of a starch for mill purposes.

SPECIAL OR TREATED STARCHES.

A number of special starches are now used which have been treated so as to make them "thin boiling starches," that is, when boiled the solution has a lower viscosity than the natural starches. These usually consist of corn starch which has been treated in some way to reduce the viscosity. The viscosities of several such starches are shown in the following table:

TABLE III.—VISCOSITIES OF SPECIAL OR TREATED STARCHES.[2]
(12 grams starch in 300 cc. water, boiled ten minutes.)

Starch	Viscosity
Eagle Finishing	1.15
N Starch alkaline	2.13
Famous N	1.17
Erkenbrecher's Modified	1.13
T. B. Crystal No. 75	1.11
T. B. Crystal No. 90	1.04
Special Warp Sizing	3.48

There are quite a number of processes for treating starches to reduce the viscosity or make them thin boiling starches. In the table above the Eagle Finishing Starch is a treated starch

[2] The samples of treated starches were very kindly furnished the author by the Corn Products Refining Co., of New York.

containing a small amount of borax and is slightly alkaline. The viscosity of the alkaline N starch has been reduced by the addition of a small amount of alkali. The other starches given in the table have been treated to reduce the viscosity and are neutral in reaction. The effect of several reagents on the viscosity of starches has been shown in a previous paper.[3]

It will be seen from this table that the viscosities of the treated starches cover quite a wide range, from a viscosity slightly less than that of corn starch to a viscosity only slightly higher than water. The Special Warp Sizing Starch is a pulverized corn starch. It is frequently claimed that pulverized starch makes a smoother size mixture than the ordinary granular starch. These treated starches, on account of having lower viscosities than untreated starches, are of value in sizing and finishing to obtain more penetration of the starch into the yarn or cloth and to increase the amount of starch which is put into the goods. This may be accomplished by using the treated starch in place of the untreated and increasing the amount used or by mixing the treated starch with the untreated starch in such proportion as to secure the desired results. For instance, in sizing or finishing if the mixture contains 50 lbs. of corn starch to 100 gallons of water and it is desired to increase the amount of starch put into the goods nearly double this amount of a thin boiling starch could be used which has a viscosity of half of that of corn starch and still obtain a size mixture with the same thickness or viscosity as with the 50 lbs. of corn starch. In other words nearly twice as much starch would be put into the yarn, thereby increasing the weight of the yarn, by using the thin boiling starch than by using the untreated corn starch. This is shown in the following formulae for sizing No. 26 yarns which are taken from actual practice:

100 gallons water
50 lbs. corn starch.

100 gallons water
95 lbs. Eagle Finishing Starch.

[3] *Journal of Industrial and Engineering Chemistry*, Vol. IV, No. 6, 1912.

It will be noted from the table of viscosities that Eagle Finishing Starch has a viscosity slightly less than half of that of untreated corn starch and hence when this starch is used the amount can be nearly doubled without effecting the penetration.

By comparing the following formula for sizing No. 26 yarns with the first formula given it will be seen how the amount of starch may be increased and at the same time obtain greater penetration and more weight than with untreated corn starch.

100 gallons water
80 lbs. Eagle Finishing Starch.

The following formula for sizing No. 26 yarns shows the use of another treated starch:

100 gallons water
65 lbs. Alkaline N Starch.

It will be noted from the table of viscosities that this starch has a viscosity of 2.13 or slightly lower than corn starch and hence a larger amount of it can be used.

In making investigations on the value of the different commercial starches for cotton mill purposes the author has received very valuable assistance from many of the cotton mills in the State. A large number of mills have very kindly sent in reports showing the kind of starch which they use and the method of preparing the starch for sizing and finishing. Below are given a number of typical formulæ for sizing by the long chain or slasher system which are in actual use by the mills. For convenience of comparison the formulæ have been calculated to a basis of 100 gallons of water. As there is such a great variety of softening agents in general use by the mills the amount of softener has not been included in the formulæ. The average amount of softener used in sizing is approximately 15 lbs. of tallow, or its equivalent, to 100 lbs. of starch or 1.5 lbs. to each 10 lbs. of starch. The amount used varies, of course, with the yarn numbers and the method of sizing.

For yarn Nos. 14 s and 20 s.

100 gallons water
66 lbs. Eagle Finishing Starch.

For yarn Nos. 14 s and 22 s.

100 gallons water
71 lbs. Eagle Finishing Starch.

These formulæ are used on practically the same yarn numbers. The first one, using 66 lbs. of starch will give greater penetration than the second, but the second formula will give more weight to the yarn.

For yarn No. 16.

100 gallons of water
63 lbs. corn starch.

In this formula, using an untreated starch, a smaller quantity of starch is used than in the other formulæ where treated starch is used.

For yarn No. 21.

100 gallons of water
62 lbs. corn starch.

For yarn No. 23.

100 gallons of water
60 lbs. corn starch.

For yarn No. 26.

100 gallons of water
50 lbs. corn starch.

100 gallons of water
95 lbs. Eagle Finishing Starch.

100 gallons of water
80 lbs. Eagle Finishing Starch.

100 gallons of water
65 lbs. Alkaline N Starch.

These formulæ for 26 s show how different starches may be used to increase the penetration and vary the amount of starch put into the yarn, thereby increasing the weight of the yarn.

For yarn Nos. 28 s and 36 s.

100 gallons water
65 lbs. Potato starch.

For yarn No. 28½.

100 gallons water
80 lbs. Famous N Starch.

For yarn No. 30.

100 gallons water
65 lbs. Famous N Starch.

100 gallons water
65 lbs. corn starch.

These formulae for 30 s show how more penetration and hence more weight may be obtained by using a thin boiling starch in place of an untreated starch.

For yarn No. 36.

100 gallons water
48 lbs. potato starch.

For yarn No. 40.

100 gallons water
65 lbs. Eagle Finishing Starch.

100 gallons water
70 lbs. potato starch.

In comparing the amounts of starch used in the different formulæ the viscosity of the different starches should be kept in mind as it will be noted that when large amounts of starch are used the treated or thin boiling starches are used in place of the untreated starch which has a higher viscosity.

In sizing by the short chain system more starch is required and a thicker solution is used than in sizing by the long chain or slasher system. This is due to the fact that the yarn is not stretched as much in short chain sizing as it is on the slashing machine and hence the starch solution penetrates the yarn more readily. For example, a size mixture composed of 120 gallons

of water, 65 lbs. starch and 8 lbs. of tallow will size about 720 lbs. of No. 14½ yarn by the short chain system, while by the slasher system the same amount of size will be sufficient for about 950 lbs. of the same yarn.

In preparing the starch for use it is very important that the size be thoroughly boiled before being used. In the reports which the author has received from the cotton mills it is always recommended to boil the size mixture from thirty minutes to one hour before using. From this it is safe to say that the size mixture should be boiled for not less than forty-five minutes before being used.

From the data which has been presented in this article it is seen that the viscosity of the starch solution is the important point to be considered in determining the value of a starch for textile purposes. There is another property of starch which is of value in the textile industry which is not shown by the viscosity, that is the finish which is imparted to the goods by the starch. Potato and cassava starch are said to produce a smooth finish, while corn and rice starch are said to produce a harsh finish. While this property may be of value in sizing and finishing some grades of goods, still no matter which one of the starches is used some softening agent must be used with it to modify the effect of the starch and it is therefore best in the majority of cases to use a cheap starch and control the finish by the use of softeners than to control the finish by varying the kind of starch used.

Sufficient data has been given to show the value of the different starches for textile purposes. There is a wide variation in the viscosity of the different starches and in the effect of boiling on the viscosities and as this is such an important factor in sizing and finishing it must be taken into consideration in selecting the starch to be used in cotton mills. As starch plays such an important part in the manufacture of cotton goods it is very important for the manufacturer to use the kind of starch which will produce the desired results most economically.

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NOTE ON THE TRANSFORMATION OF AMMONIUM CYANATE INTO UREA.*

Chattaway[1] says, "The course of the reaction which takes place when ammonium cyanate is transformed into carbamide has never been satisfactorily explained. Up to a few years ago it was universally regarded as a peculiar case of isomeric change and no consideration was given to the process by which the conversion was effected." He then states that various specified reactions of carbamide, cyanic acid, isocyanic acid and their esters may be simply explained "by regarding them as instances of the well known tendency of the carbonyl group to add groups such as R_2NH and ROH, followed by a subsequent atomic rearrangement involving only the transference of a hydrogen atom from an oxygen atom to a nitrogen atom connected with it through the doubly linked carbon atom, thus:

$$N:C:O \rightarrow \cdot N:C\begin{matrix}OH\\ <\\ N:\end{matrix} \rightarrow \cdot NH\cdot CO\cdot N:$$

The conversion of ammonium cyanate into carbamide should therefore be formulated as follows:"

$$NH_4\cdot N:CO \rightleftarrows H\cdot N:C:O + NH_3 \rightleftarrows H\cdot N:C\begin{matrix}OH\\ <\\ NH_2\end{matrix} \rightleftarrows H_2N\cdot CO\cdot NH_2$$

The three stages, then, in the transformation are (1) the breaking up of ammonium cyanate into cyanic acid and ammonia, (2) the formation of an addition compound, and (3) a rearrangement of this compound.

A simpler explanation eliminates this addition compound and its rearrangement. I find in my note book on the lectures in Organic Chemistry by Professor H. B. Hill at Harvard University in 1896, this statement: Ammonium cyanate breaks up with heat into HNCO and NH_3 and then the NH_3 adds itself as follows:

$$\begin{matrix}H.N:C:O\\ \uparrow\ \ \uparrow\\ H\ NH_2\end{matrix} = H_2N\cdot CO\cdot NH_2$$

* Reprinted from *The Journal of the American Chemical Society*, Vol. XXXIV, No. 9, September, 1912.

I have used this explanation in my own lectures since that time. Essentially the same explanation is given by Willstätter in his lectures in Zürich. By introducing the idea of partial valence the mechanism is more readily conceived. The reaction is formulated thus:

The partial valences of the nitrogen and carbon atoms are represented by a number of very short lines, not dots, which should be reserved for ordinary valences. (The practise of writers in this matter is not uniform, but uniformity would be very desirable.) When the partial valences come into play in the presence of $H.NH_2$, one of the double bonds between nitrogen and carbon is broken, as represented in lecture practise by a double stroke across the bond and the partial valences resolve themselves into ordinary valences.

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NEW THERMOMETERS FOR MELTING POINT DETERMINATION.*

Uniformity in practise in making melting point determinations would be very desirable, for even to-day there are too many cases where different observers disagree. The failure to agree is not always due to the quality of the material if we may have confidence in the analytical data given. Many forms of apparatus are in use as well as various kinds of thermometers. Other factors also enter in. The practise of reporting the corrected reading is a step in the right direction and its extension should be constantly urged.

In order to avoid the necessity of making corrections for the exposure of the mercury column I have devised a thermometer with a short scale, so that it may be completely immersed in the bath. The method of construction may be readily seen from the accompanying sketch. Owing to the compact form of the scale it was necessary to construct a set of seven thermometers, each with a milk glass scale of 50° with divisions in degrees. The length of the scale is 35 mm. The thermometer jacket is lengthened so that the total length is 20 cm. This permits of its suspension by means of a cork as in the Thiele apparatus which is a particularly good form to be used with this thermometer. The mercury bulb is small and compact and above it is a constriction to enable one to attach the capillary tube if that is desired. For the protection of the manufacture of the thermometers patent No. 507,320 has been entered in the German Patent Office. The thermometers may be obtained from C. Richter, 30 Lehrterstrasse, Berlin, N. W. 5.

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